

Preparation and Properties of Allylsucrose 408

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Allylsucrose can be prepared economically by the use of allyl chloride. Allylsucrose, both as prepared and partially polymerized (blown) in organic solvents, can be stored without change for a long time. Some data on accelerated weathering tests are given. The gelation time can be considerably shortened by making a methacrylyl derivative or by mixing allylsucrose with some acrylic and methacrylic esters.

THE practical possibilities of utilizing allylsucrose (5) proved of sufficient interest to the sugar and synthetic coating industry to warrant further investigation. Allyl ethers of sucrose have been described by several investigators (1, 4, 5, 7, 8). Sucrose with allyl substitution from four to eight groups was made by various methods, but optimum conditions for the preparation of allylsucrose with either allyl bromide or allyl chloride have not been published. The properties of allylsucrose, particularly its ability through oxidative polymerization to change into an insoluble and infusible resin, suggested a number of practical applications, such as coating compositions to produce resistant films. Previous articles on the subject, however, gave little information on the properties of such films. In this article optimum conditions for the preparation of allylsucrose are indicated, and the preparation and properties of allylsucrose films are described.

PREPARATION

ALLYL BROMIDE METHOD. Nichols and Yanovsky (5) used twice the theoretical amount (16 moles) of allyl bromide required for complete substitution of sucrose. By varying the amount of allyl bromide, the results in Table I were obtained.

TABLE I. PREPARATION OF ALLYLSUCROSE WITH ALLYL BROMIDE

Moles per Mole Sucrose		Analysis of Product		Yield, % of Theoretical
Allyl bromide	Alkali	Allyl groups	Hydroxyl groups	
4	4	6.1	...	27
8	8	6.0	...	74
12	12	6.7	1.2	91
16	16	6.7	1.2	88

Therefore, 12 moles of allyl bromide and an equivalent amount of alkali appear to represent the optimum ratio of reagents. Based on this fact and other minor improvements over the previous method, the preparation of allylsucrose was carried out as follows:

Two hundred grams of sucrose (0.6 mole) were added with stirring to 562 grams of 50% sodium hydroxide (7.0 moles) in a 2-liter, round-bottomed, three-necked flask equipped with a reflux condenser, stirrer, and dropping funnel. To this mixture 848 grams (7.0 moles) of allyl bromide were added dropwise with constant stirring, over a period of 2 to 3 hours, while the temperature of the bath was maintained at 72° to 78° C. After all the allyl bromide was added, the reaction mixture was heated at 80° C. for 3 hours. Water was then added to dissolve the sodium bromide. The upper organic layer was separated and steam-distilled. The crude allylsucrose was covered with cold water in a tall cylinder. Cold water was bubbled through the product until the wash water, flowing from a simple constant-leveling device attached to the top of the cylinder, was neutral and showed a negative test for halogen with silver nitrate. The product was then dissolved in

toluene; the wet toluene solution was decolorized with activated carbon, dried over anhydrous sodium sulfate, filtered, and concentrated at reduced pressure (in an atmosphere of nitrogen) at a maximum bath temperature of 100° C. The yield of light yellow oil was 325.8 grams (91.3% of the theoretical yield) with a refractive index (n_D^{20}) of 1.4879. It contained 6.7 allyl groups and 1.2 hydroxyl groups.

The lower aqueous layer of the reaction mixture was extracted with ether; the ethereal extract was dried over anhydrous sodium sulfate, filtered, and then fractionated. After removal of the ether, 8 grams of allyl alcohol, which accounted for 4.5% of the excess allyl bromide, were collected. The undistilled residue consisted of 4 grams of a light-yellow oil (n_D^{20} 1.4800), which represented a 1.1% yield of allylsucrose.

The organic layer in the steam distillate was salted out with sodium chloride, dried over anhydrous sodium sulfate, and fractionated. The diallyl ether obtained, 94.8 grams, accounted for 62.5% of the excess allyl bromide. Calculations for recovery of excess allyl bromide were based on the assumption that allylsucrose contained 6.7 allyl groups.

ALLYL CHLORIDE METHOD. Two autoclaves were used. One was glass-lined with iron fittings, the other Monel metal. The amount of allyl chloride (and equivalent amount of alkali) was varied in an attempt to find the optimum ratio of reagents. Table II gives the results.

TABLE II. PREPARATION OF ALLYLSUCROSE WITH ALLYL CHLORIDE

Autoclave	Moles Allyl Chloride/Mole Sucrose	Analysis of Product			Yield % of Theoretical
		Allyl Groups		Hydroxyl groups	
		Direct	From hydroxyl		
Monel	8	4.7	5.7	2.3	70
Monel	10	4.8	6.1	1.9	81
Monel	12	5.2	6.3	1.7	90
Glass	12	5.8	6.1	1.9	84
Monel	16	5.5	6.6	1.4	90

As with allyl bromide, apparently the optimum amount of allyl chloride is 12 moles per mole of sucrose. Allylsucrose was prepared as follows:

1. Sucrose (1000 grams, 2.9 moles) was added with mechanical stirring to a mixture of 1402 grams (35.0 moles) of sodium hydroxide and 700 ml. of water at room temperature in a 2-gallon, glass-lined autoclave equipped with a stirrer and a jacket connected to steam and cold water inlets. Allyl chloride (2680 grams, 35.0 moles) was then added, and the autoclave was sealed and heated to 85° C. (jacket temperature). At the beginning of the reaction and up to about 45° to 50° a valve at the top of the autoclave remained open until the vapors of allyl chloride started to condense at the tip of the valve. Heating during the initial stage of the reaction was carefully controlled, since the reaction is exothermic and a rise in temperature above 83° C. darkens the product considerably. Within 1.5 hours the thermometer well temperature was 82° C., and the internal pressure increased rapidly to 20 pounds per square inch. At this point cold water was circulated through the jacket to moderate the reaction. After this exothermic stage was passed, the well temperature was easily controlled at 80° to 82° C. for 5.5 hours longer. At the end of 8 hours the well temperature was 81° C., and the pressure was down to about 4 pounds. Heating was discontinued at this point, and the autoclave was allowed to cool. The autoclave was then opened and filled with water, with stirring, to dissolve the sodium chloride. The organic layer was separated, steam-distilled, washed with water, and treated as described for the allyl bromide preparation. The yield of light brown oil was 1400

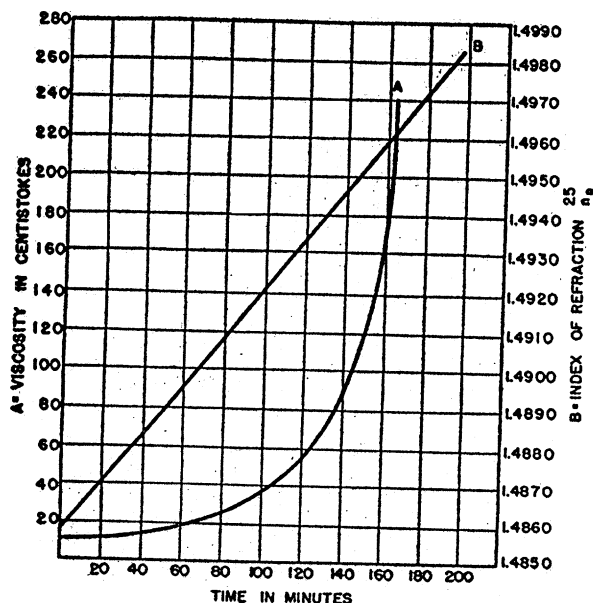


Figure 1. Polymerization of Allylsucrose at 100° C.

grams (83.5% of theoretical) with a refractive index (n_D^{25}) of 1.4920. It contained 5.8 allyl groups and 1.9 hydroxyl groups.

2. Sucrose (500 grams, 1.5 moles) was added with motor stirring to a mixture of 701 grams (17.5 moles) of sodium hydroxide and 350 ml. of water at room temperature in a 1-gallon, jacketed, Monel metal autoclave. Allyl chloride (1340 grams, 17.5 moles) was added, and the autoclave was sealed and heated to 85° C. (jacket temperature) for 8 hours. Because of the better heat transfer of this autoclave, it was not necessary at any time to cool the jacket to moderate the reaction. Within 1.75 hours the internal pressure reached 25 pounds per square inch, and the well temperature was 82° C. At the end of 8 hours the pressure was down to about 4 pounds and the well temperature was 78° C. The autoclave was then cooled and filled with water to dissolve the sodium chloride, and the product was treated as described above. The yield of light brown oil was 783 grams (90% of theoretical), $n_D^{25} = 1.4960$. The number of allyl groups was 5.2; the number of hydroxyl groups, 1.7.

The allyl content was determined as described previously (4); the hydroxyl content was determined by the method described by Ogg, Porter, and Willits (6).

Tables I and II show that for the allyl bromide preparation and for the glass-lined autoclave method the sum of the allyl and hydroxyl groups approximates 8, as was expected. In other words, the allyl substitution, whether found directly or from the hydroxyl determination, is about the same. On the other hand, for batches made in the Monel metal autoclave the two values are different, and the difference is entirely outside the experimental error¹ admissible in such determinations. Thus, for a batch made in the glass-lined autoclave with 12 moles of allyl chloride, the allyl substitution by direct determination was 5.8 groups, and from the hydroxyl determination 6.1 groups, the two results being within experimental error. On the other hand, for a similar batch made in the Monel metal autoclave there were 5.2 and 6.3 groups, respectively. This discrepancy in allyl values for the preparation made in a Monel metal autoclave can be explained by the difference in gelation time of allylsucrose preparations of vary-

¹ The discrepancy between the substitution calculated from unsaturation and hydroxyl determinations for allylsucrose was originally communicated by J. Robert Roach of General Mills, Inc.

ing allyl content. It has been shown (9) that allylmannitol with a high allyl content gels faster than that with a lower degree of allylation. The same rule holds true for allylsucrose. An allyl bromide preparation with 6.7 allyl groups (1.2 hydroxyls) gelled in 205 minutes at 100° C.; allylsucrose made in a glass-lined autoclave with 5.8 allyl groups (1.9 hydroxyls) gelled in 250 minutes; finally, allylsucrose made according to the Tomecko and Adams method (8) with 4.4 allyl groups (3.5 hydroxyls) gelled in 300 minutes. On the other hand, a product made in a Monel autoclave with 4.9 allyl groups (2.2 hydroxyls) gelled in 180 minutes. This gelation time is too short even if the allyl content is calculated from the hydroxyl determination, which will make it 5.8 allyl groups. The rapid gelation of the Monel autoclave product can be explained on the assumption that allylsucrose with 5.8 allyl groups was partially polymerized, since polymerization is always accompanied by the decrease in unsaturation. This assumption was further substantiated by the molecular weight determination (freezing point depression of benzene solutions) for various preparations of allylsucrose. The molecular weight of allylsucrose (6.7 allyl groups) made with allyl bromide was 584 and 578 (theoretical value, 611); the molecular weight of the product made in a glass-lined autoclave was 660 and 689 (theoretical value, 575). On the other hand, the Monel autoclave preparation had a molecular weight of 924 to 948, as compared with the theoretical value of 575.

The catalytic polymerization of allylsucrose in the Monel metal autoclave was probably due to one of the constituents of Monel metal. For coating applications this partial polymerization would not be harmful and, in fact, might be beneficial, since the usual procedure is to blow (partially polymerize) the material before dissolving it in turpentine or other solvents. It is possible, however, that in some applications the use of the monomer will be preferable. In that case a glass-lined autoclave or an autoclave of some other material (perhaps stainless steel) should be used.

The experiments described above were carried out with commercial sucrose. The following results were obtained with raw sugar. The product made in a glass-lined autoclave with 12 moles of allyl chloride had 5.7 allyl groups by direct determination, 6.3 allyl groups by hydroxyl determination, and 1.7 hydroxyl groups; the yield was 80% of the theoretical. The product made in the Monel metal autoclave had 5.2 allyl groups by direct determination, 6.1 allyl groups by hydroxyl determination, and 1.9 hydroxyl groups; the yield was 90% of theoretical. Comparison of these data with those obtained for commercial sucrose (Table II) shows that the results are almost identical. The color of the product obtained from raw sugar was only slightly darker than that of the product obtained from sucrose.

POLYMERIZATION

A previous article (5) pointed out that for some applications—for example, coating materials—it is advisable to oxidize the product partially to increase viscosity. Since, during this partial polymerization, the refractive index increase parallels the increase in viscosity, by observing the change in refractive index and interrupting the oxidation at a standard value, uniform results

TABLE III. CHANGE IN REFRACTIVE INDEX OF ALLYLSUCROSE DURING STORAGE

Sample No.	Refractive Index, n_D^{25}							
	At start	5 weeks	10 weeks	18 weeks	26 weeks	32 weeks	43 weeks	52 weeks
1	1.4848	1.4847	1.4848	1.4848	1.4849	1.4851	1.4853	1.4857
2	1.4890	1.4892	1.4899	1.4901	1.4906	1.4909	1.4910	1.4910
3	1.4900	1.4904	1.4909	1.4913	1.4920	1.4922	1.4928	1.4930
4	1.4911	1.4913	1.4919	1.4925	1.4931	1.4938	1.4942	1.4944
5	1.4920	1.4925	1.4930	1.4937	1.4948	Gelled
6	1.4930	1.4933	1.4940	Gelled
7	1.4941	1.4947	1.4948	Gelled
8	1.4949	1.4950	Gelled
50% soln. of No. 7 in								
Turpentine	1.4701	1.4702	1.4703	1.4703	1.4705	1.4708	1.4709	1.4709
Toluene	1.4937	1.4941	1.4940	1.4940	1.4941	1.4946	1.4950	1.4953

will be obtained. Figure 1 shows the viscosity and refractive index curves for a laboratory batch of allylsucrose made with allyl bromide. Since laboratory preparations are fairly well standardized with regard to allyl content, viscosity, refractive index, and gelation time, reproducible results were obtained whenever the partial polymerization was interrupted at the same refractive index.

Allylsucrose prepared in a glass-lined autoclave with allyl chloride has a lower allyl content than the products prepared with allyl bromide and, hence, gives different values for viscosity, refractive index, and gelation time. The viscosity-refractive index curves will, therefore, be somewhat different from those in Figure 1 but will serve the same purpose. The curves for allylsucrose made in a Monel metal autoclave will also be different for, in addition to having a different degree of allylation, the product will be partially polymerized.

The point at which the preliminary polymerization is stopped is determined by two factors. The closer the refractive index is to the gelation point, the quicker will the film of allylsucrose become tack-free on exposure to air. Thus a 50% solution of allylsucrose in toluene or turpentine (having a refractive index of 1.4940) with 0.1% of cobalt (as naphthenate or octoate) dried tack-free in 60 to 90 minutes at room temperature. On the other hand, allylsucrose, particularly when partially polymerized, has a tendency to polymerize and eventually gel, even at room temperature. It is important, therefore, to know how long the polymerized substance will be kept before use.

The effect of storage on monomeric and partially polymerized allylsucrose was investigated. Allylsucrose (6.7 allyl groups) was polymerized at 100° C. At several points (Figure 1) 25-cc. samples were withdrawn, put into glass vials closed with plastic screw caps, and stored on a laboratory shelf at room temperature (about 25° C.). From time to time the index of refraction of each sample was examined. Table III gives the results.

Table III shows clearly that, whereas the allylsucrose as prepared (sample 1) scarcely changed during a year of storage, the partially polymerized samples of refractive index 1.4920 or higher gelled at various intervals during this period; the sample of refractive index 1.4911 closely approached the gelation point after 12-month storage. Although sample 7 gelled in about 4 months, 50% solutions of the same samples in toluene and turpentine showed no sign of gelation after a year of storage.

WEATHERING TESTS

It has been shown that allylsucrose, as prepared or partly polymerized and dissolved in organic solvents, can be kept for a long time without deterioration. In addition the resistance of allylsucrose films to light and water was briefly investigated. Wood panels, 4.5 × 2 × 0.25 inch, were given two coats of the various allylsucrose solutions described in Table IV. Both oak and pine were used for panels 25 to 33; for the rest, only pine panels were used. In all tests except 51, allylsucrose made with allyl bromide was used. In test 51 allylsucrose prepared in an autoclave with allyl chloride was used. After drying, the panels were inserted in an Atlas Twin-arc Weatherometer, where they were exposed to the radiation of the arcs only. The water spray was omitted. The temperature of the panels was approximately 50° C.

After 900-hour exposure the only badly checked samples were pine and oak panels of test 30. No other panel showed lifting or checking to the naked eye. In some of the oak panels the filler failed before the coating. The best looking panels were 27, 28, 43-48, 50, and 51. Panel 45 was dull, owing to the excess of plasticizer. Highest gloss was obtained with 5% of plasticizer. Panels 50 and 51, containing no plasticizer, were equal to the best samples.

All panels except 30 were then put back in the Weatherometer and exposed to the action of both the arcs and the water spray. After 24 hours all but samples 31, 43-48, and 50 had failed. After 48 hours the rest of the panels had failed.

GELATION OF ALLYLSUCROSE AND DERIVATIVES

Since for some uses allylsucrose has to be partly polymerized (blown), a time-consuming process, it was deemed advisable to prepare some related polymerizable derivatives of sucrose and of allylsucrose and to determine their gelation time. Methallylsucrose (methallyl 6.0 groups, hydroxyl 1.7 groups) was prepared according to the method of Nichols, Wrigley, and Yanovsky (5). Crotylsucrose (crotyl 6.2, hydroxyl 1.5 groups) was prepared in a similar manner. Crotyl bromide was made according to the method of Juvala (2). The gelation time for methallylsucrose was 465 minutes; for crotylsucrose, 2175 minutes. Both compounds gelled considerably more slowly than allylsucrose.

TABLE IV. SOLUTIONS USED FOR WEATHERING TESTS

Panel No.	Blown Allyl-Sucrose in Soln., %	Solvent	Plasticizer (Based on Allylsucrose), %	Drying Time (Loss of Tack) at Room Temp., Min.
25	50	Ethyl alcohol	...	90
26	65	Same	...	90
27	50	Toluene	...	90
28	65	Same	...	95
29	50	Ethyl acetate	...	73
30	65	Same	...	73
31	50	n-Butyl alcohol	...	76
32	65	Same	...	76
33	50	Turpentine	...	90
34	65	Same	...	93
35	50	Mixed lacquer solvent	...	78
36	65	Same	...	78
37	50	Turpentine + ethyl acetate (1:1)	...	88
38	65	Same	...	88
43	50	Turpentine	Boiled linseed oil, 5	74
44	50	Same	Same, 10	80
45	50	Same	U.S.P. castor oil, 40	100
46	50	Same	Same, 20	94
47	50	Same	Same, 10	90
48	50	Same	Dehydrated castor oil, 5	111
50	50	Same	...	94
51	50	Same	...	94

These data show that compounds closely related to allylsucrose, such as crotyl- and methallylsucrose, polymerize even more slowly than allylsucrose. Likewise, addition of a benzyl and butyl group to allylsucrose retards the gelation time of the latter. On the other hand, introduction of a methacrylyl group considerably reduces the polymerization time of allylsucrose.

Two mixed sucrose ethers were prepared, allylbutyl- and allylbenzylsucrose.

Allylbutylsucrose was prepared in the following manner: To a well-stirred mixture of 50 grams (0.15 mole) of sucrose and 166 grams of 50% sodium hydroxide solution in a two-necked, 1-liter, round-bottomed flask equipped with a reflux condenser and a dropping funnel, 110 grams (0.6 mole) of butyl iodide were added dropwise. The reaction mixture was stirred at 100° C. for 1 hour, then 103 grams (2.6 moles) of sodium hydroxide pellets and 121 grams (0.7 mole) of butyl iodide were added. The temperature of the reaction was raised to 110° for 30 minutes, then to 115° for 1 hour. The mixture was cooled to 100°, and 181 grams (1.5 moles) of allyl bromide were added dropwise. The mixture was then heated at 115° C. for 2 hours, cooled to room temperature, and treated with sufficient water to dissolve sodium iodide and bromide. The organic layer was separated, steam-distilled, washed with water in a tall cylinder, and dissolved in ether. The ethereal layer was washed with sodium thiosulfate solution, then with water, and was finally dried over anhydrous sodium sulfate, filtered, and concentrated at reduced pressure under nitrogen. The yield of light brown oil was 34.8 grams (n_D^{20} 1.4801). Analysis showed 6.7 allyl groups, 0.9 butyl group, and 0.4 hydroxyl group.

Allylbenzylsucrose was prepared as follows: To 166 grams of a 50% solution of sodium hydroxide, 50 grams of sucrose were added, with stirring, at 70° to 80° C. At 110° to 115° C. 19 grams of benzyl chloride were added dropwise, and then the reaction mixture was heated at 115° for 2 hours. It was then cooled to 90°, and 218 grams of allyl bromide were added dropwise. The heating was continued for 3 hours. The reaction mixture was then cooled and treated as described for the preparation of allylsucrose. The yield of light brown oil was 46 grams (n_D^{20} 1.5090). Analysis showed 6.1 allyl groups, 1.0 benzyl group, and 0.9 hydroxyl group.

TABLE V. GELATION OF ALLYLSUCROSE IN THE PRESENCE OF ACRYLIC AND METHACRYLIC ESTERS

Allylsucrose + equal amount of:	Gelation Time, Min.
Methyl methacrylate	210
<i>m</i> -Tolyl acrylate	197
Butyl methacrylate	135
Phenyl methacrylate	106
2-Ethyl hexyl acrylate	87
Octyl methacrylate	69
Isopropoxy ethyl acrylate	51
Cyclohexyl acrylate	38
Tetrahydrofurfuryl methacrylate	37
	19

The gelation time for allylbutylsucrose was 300 minutes, and for allylbenzylsucrose, 590 minutes. Both compounds gelled considerably more slowly than allylsucrose.

Methacrylyl ester of allylsucrose was prepared by dissolving incompletely allylated sucrose in pyridine and treating it with methacrylic anhydride. The resulting yellow viscous liquid (n_D^{25} 1.4788) contained 6.7 allyl groups and 1.2 methacrylyl groups. It gelled in 78 minutes. The original allylsucrose gelled in 205 minutes. The mixture of equal parts of the original allylsucrose and this allylmethacrylylsucrose gelled in 146 minutes, the average time for the two products.

Since methacrylyl groups added to the allylsucrose molecule shorten considerably the gelation time of the product, it seemed appropriate to determine whether the mere addition of esters of acrylic and methacrylic acid will not produce the same result, perhaps through copolymerization of the two compounds. The results are summarized in Table V.

Methyl methacrylate had little effect in reducing the gelation time of allylsucrose because the gelation experiments were carried out at 100°C., and most of the ester, which boils at 100°, evaporated from the mixture. When the esters of higher-boiling point were used, the gelation time was reduced considerably.

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